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Research paper

Synthesis, structure and properties of poly(L-lactide-co- ϵ -caprolactone) statistical copolymers

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ABSTRACT

Four poly(L-lactide-co- ϵ -caprolactone) (PLCL) copolymers were synthesized at 120, 130, 140 and 150 °C by ring opening polymerization using stannous octoate catalyst at a 2000:1 comonomer:catalyst ratio. Gel permeation chromatography (GPC) and ¹H NMR measurements were performed to determine the molecular weight, composition and chain microstructure of copolymers of L-lactide(LA): ϵ -caprolactone(CL) synthesized using 90:10, 80:20, 75:25 and 70:30 feed ratios. The overall conversion of these PLCL copolymers was in the range of 80%–90% leading to weight average molecular weights (M_w) between 98,500 and 226,000 g mol⁻¹ depending on feed composition and polymerization temperature. At temperatures lower than 140 °C, the incorporation of CL units into polymer chains was incomplete because of the low reactivity of CL, thus at 120 °C the copolymer composition was difficult to control obtaining more LA in the copolymer than the desired, hence the blocky character of PLCL copolymers also increased. At 150 °C the catalyst was less effective and the molecular weights of the copolymers took lower values. A temperature of 140 °C was established as optimal to obtain highest yields and molecular weight. The number average crystallizable lactide sequence lengths (l_{LA}) shifted from 6.5 to 16.7 LA repeat units for PLCL polymerized at 140 °C while the randomness character (R) value shifted from 0.4 for polymerization at 130 °C to 0.6, at 150 °C. Increasing the LA content in the copolymers the glass transition temperature and the crystallizability and melting temperature of PLCLs approached to that of PLLA homopolymer. The aging sensitivity of PLCLs increased with CL content. A double T_g behavior due to phase separation associated to crystallizing LA blocks was observed during aging. The mechanical properties, however, evolved toward the PLLA character when the molar content of LA in PLCL was increased from 66% to 90%, observing a shift from an elastomeric thermoplastic behavior to that of a glassy plastic, reflected by an increase in tensile modulus (from 12.0 to 1343.1 MPa) and a decrease in strain recovery after break (from 93.5% to 25.0%). Small amounts of CL content in the copolymers produced large

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improvements in their deformability with regard to PLLA. In addition, thermogravimetric analysis demonstrated that PLCLs are more stable to thermal degradation than PLLA and they undergo a more complex degradation mechanism than those of the corresponding homopolymers.

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1. Introduction

In the last decade, the synthesis of biodegradable polymers has been stimulated to fill the needs of new materials in the regenerative medical science. Polyesters synthesized from ring-opening polymerization (ROP) of cyclic ester monomers (Jerome and Lecomte, 2008; Albertsson and Varma, 2003) (lactones and dilactones) have found wide applications in temporary implants used in surgical procedures of osteosynthesis, surgical threads and fibers, controlled-release drug carriers, scaffolds in tissue engineering and medical devices like catheters in urology and stents in cardiology. In addition to tin (II) octoate, extensively used in the synthesis on a large scale of resorbable polymers (Stjerndhal et al., 2007), other metal-containing catalysts have been studied for the ROP of lactide (LA), glycolide (GL), ring-strained lactones and cyclic carbonates. These include zinc or aluminum alkoxides (Dechy-Cabaret et al., 2004; O'Keefe et al., 2001; Barakat et al., 1991; Baran et al., 1997; Ovitt and Coates, 2002), rare earth metal compounds (O'Keefe et al., 2001; Ovitt and Coates, 2002; Shen et al., 1996; Ravi et al., 2001; Chamberlin et al., 2000) and bismuth catalysts (Kricheldorf, 2009). Some of these catalysts also raise health safety concerns. Enzymatic ROP of lactones, lactide (LA) and glycolide (GL) has also been studied to address attention about possible toxicity of heavy metal catalyst and initiators (Albertsson and Srivastava, 2008).

The most often employed polymers are aliphatic polyesters based on lactide (LA), glycolide (GL), ϵ -caprolactone (CL) and polyethylene glycol (PEG). However, most of the absorbable polymers studied today, e.g. poly(L-lactide) PLLA (Auras et al., 2004; Sarasua et al., 1998; Gupta and Kumar, 2007; Garlotta, 2001), display a very similar mechanical behavior, with high elastic modulus and rather low elongation at break values, due to their high glass transition temperature and crystallinity. These materials are, therefore, clearly inappropriate for numerous clinical uses, where highly flexible biodegradable materials are required (Cui et al., 2011; Lipik et al., 2010). This unsuitability shown by polylactides (PLA) might be overcome by blending or copolymerization with lower glass-transition temperature polymers, such as poly(ϵ -caprolactone) (PCL), which presents a glass transition temperature at -60°C (Labet and Thielemans, 2009). Unfortunately, the degree of miscibility of PLA and PCL is poor, due to their lack of specific interactions, thus phase separation results. The adhesion forces at the interphase of the PLA–PCL blends are too weak and, in this way, the desired stress transmission across the interphase is not efficient and thus poor mechanical properties are obtained (Zhang et al., 2006; López-Rodríguez et al., 2006).

Copolymerization of lactide with ϵ -caprolactone can be an appropriate method for the control of mechanical properties, shape-memory behavior, degradation rate and controlled drug-release properties, which, thereby, widens the potential for biomedical applications of PLLA. Hence, the synthesis of diblock, triblock, multiblock or random poly(L-lactide-co- ϵ -caprolactone) (PLCL) copolymers is of great interest. Nevertheless, phase separation significantly affects the properties of diblock and triblock copolymers (Liu et al., 2009; Qian et al., 2000; Kim et al., 2001). This disadvantage could be solved by simultaneous copolymerization of the two comonomers, the technique employed in this work, or by treating PLA and PCL with chain extender reagents (Jeon et al., 2003; Cohn and Hotohely-Salomon, 2005; Teng et al., 2004).

When synthesizing statistical copolymers, depending on the polymerization conditions and the relative rates of incorporation of each comonomer, copolymers exhibit different chain microstructures following different distributions of sequences. Grijpma and Pennings (1991) were the first authors who reported that, varying the polymerization temperature, PLCL copolymers have different average sequence lengths. NMR signals can be easily assigned to the different dyads of the PLCL (Kasperczyk and Bero, 1991) providing a way to calculate the number-average sequence lengths (l_i) of LA and CL building blocks. These values are usually compared to the Bernoullian random number-average sequence lengths (l_i)_{random} (Herbert, 1993) obtaining the randomness character value (R), which is commonly used as a comparative parameter in the chain microstructure discussion.

Different catalysts and initiators (Feng et al., 1983; Kricheldorf et al., 1988; Vanhoore et al., 1992; Stevels et al., 1996; Simic et al., 2000) were utilized at various polymerization temperatures with different reaction times and amounts of catalyst (Jeon et al., 2003; Grijpma and Pennings, 1991; Tsutsumi et al., 2009; Kricheldorf et al., 1992; Garkhal et al., 2007; Nalampang et al., 2007; Jeong et al., 2004), but an agreement was not reached with regard to the optimal conditions for the synthesis of PLCL. Some authors used solvent in the reaction (Kwon et al., 2005; Lee et al., 2008) but in this study the copolymers were prepared by ROP in bulk, avoiding the removal step of the toluene once the reaction completed. Herein, statistical PLCL copolymers of different comonomer compositions were synthesized using 90 : 10, 80 : 20, 75 : 25 and 70 : 30 feed ratios at temperatures ranging from 120°C to 150°C , the temperature range in which the tin (II) octoate catalyst-initiator in cyclic esters polymerization is considered to be more effective (Kricheldorf and Serra, 1985). The reaction was carried out by simultaneous addition of the LA and ϵ -CL while the comonomers:catalyst molar ratio was 2000 : 1 (Lu et al., 2008). 24 h of reaction time was necessary to achieve substantial conversion of the CL

monomer, because of the fact that the growing chain end, whether it is lactoyl- or caproyl-based, is more reactive toward LA than CL (Moravek and Storey, 2009). Yields of reaction, thermal properties, molecular weight distribution, and composition and microstructure of the copolymers were investigated by means of differential scanning calorimetry (DSC), gel permeation chromatography (GPC) and proton nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$).

The microstructural control is particularly relevant to the tailoring of copolymer properties but it is usually forgotten when developing new biomaterials for medical uses and judging their behavior. In the present work, thermogravimetric analysis, mechanical properties and the effects of physical aging were evaluated for the copolymers synthesized at 140 °C, that is, the PLCLs of different LA content showing a randomness character (R) around 0.5. Hence, our studies will be conducted in terms of copolymer composition, ignoring the small differences between the randomness character of each copolymer.

Nalampang et al. (2007) studied earlier the thermal stabilities of their PLCLs obtained by one-step and two-step procedures. The degradation temperature range of PLCL copolymers increases with the CL content improving the features of PLLA. However, many few researchers had paid attention to the thermal decomposition mechanisms of PLCL. On the other hand, Lu et al. (2008) made a great work analyzing the shape memory properties of PLCL copolymers of different compositions but did not treat the mechanical properties in depth. In addition, the chain microstructure of their materials was not characterized. Finally, concerning physical aging, Tsuji et al. (2000); Saha and Tsuji (2006), after studying the behavior of PLCL 5050 and PLCL 8218, demonstrated that PLCLs changed their physical properties during storage at 37 °C. In this work, in an attempt to study in more detail the aging effect of PLCL, films of different compositions were prepared and stored at room temperature (21 ± 2 °C) monitoring the crystallization and phase structure evolution by DSC and measuring the mechanical properties at different times of aging.

2. Experimental details

Materials

L-lactide monomer (assay >99.5%) with <0.02% of water content was obtained from Purac Biochem (The Netherlands). ϵ -caprolactone monomer (99% assay) was provided by Alfa Aesar GmbH & CoKg (U.S.A.). Stannous octoate, also known as tin (II) octoate, stannous 2-ethylhexanoate or bis(2-ethylhexanoate)tin (assay 95%), was supplied by Sigma Aldrich. The methanol and chloroform were respectively purchased from Prolabo and Panreac and utilized as received. PLLA of 498,000 g mol $^{-1}$ of weight average molecular weight (M_w) and 1.61 of polydispersity, was used in this work to compare its properties with that of the synthesized PLCL copolymers, and was also provided by Purac Biochem.

Synthesis of statistical poly (L-lactide-co- ϵ -caprolactone)

The synthesis reaction of Fig. 1 was carried out in a 50 mL flask, immersed in a controlled temperature oil bath. In each

polymerization, predetermined amounts of LA and ϵ -CL were simultaneously added and melted. The flask was purged for 30 min with a nitrogen stream under the surface of the melt. Then, the stannous octoate was added using a 2000 : 1 comonomers:catalyst molar ratio. The magnetic stirrer was maintained at 100 rpm. After 24 h of reaction, the product was dissolved in chloroform and precipitated pouring the polymer solution into excess of methanol in order to remove the catalyst impurities and the monomers that did not react. Finally, the product was dried at 45 °C under vacuum until it reached constant weight.

Thermal properties

The thermal properties were determined on a DSC Q200 (TA Instruments) calibrated with pure indium and sapphire standards. Samples of 5–9 mg were cooled at -90 °C and heated to 210 °C at 20 °C min $^{-1}$, erasing their thermal history. This first scan was used to determine the melting temperature (T_m) and the heat of fusion (ΔH_f) of the precipitated copolymers. The degree of crystallinity (x_c) was calculated assuming that only the lactide units crystallize. Then, a second scan was made from -90 to 210 °C at 20 °C min $^{-1}$ to determine the glass transition temperatures (T_g) from the inflection point of the heat flow curve.

Differential scanning calorimetry (DSC) was also employed to carry out a monitoring of the physical aging of films of the PLCLs synthesized at 140 °C. The study of the thermal properties was performed by means of a scan from -90 to 210 °C at 20 °C min $^{-1}$. The glass transition temperature (T_g), and its associated specific heat change (ΔC_p), and the enthalpy relaxation (δ_H) were determined for nascent samples and for samples aged for predetermined periods. The increase in the crystallinity of the films aged at room temperature (21 ± 2 °C) was followed by measurements of the heat of fusion.

Molecular weight measurements

Gel permeation chromatography (GPC) measurements were performed with a Waters 1515 chromatograph apparatus equipped with a Waters 2414 refractive index (RI) detector. The Styragel columns were calibrated with polystyrene standards at 50 mV of signal. Chloroform was used as the mobile phase at a flow rate of 1.0 mL min $^{-1}$. Weight average molecular weights (M_w) and polydispersity (P.I.) data of the synthesized PLCL copolymers were obtained from their molecular weight distribution curve at a RI peak height in the range of 40 to 60 mV.

It is worth to consider that the injected mass (injection volume and concentration) affects both the peak position (retention volume) and the peak shape (height of RI signal). The optimum concentration and injection volume depends on the sample itself. High molar masses lead to high-solution viscosities hindering the diffusion process on the column. When it happens, higher elution volumes are measured and lower molecular weights are calculated. This problem is less pronounced for low molecular weights and narrow samples. Calibrating at the same signal (50 mV) and measuring in the range of 40 to 60 mV, where the peak position stay almost constant, seems to be an accurate way to determinate the molar weights.

Fig. 2 shows the GPC curves of PLCL copolymers synthesized at 140 °C. There is a single peak on each GPC

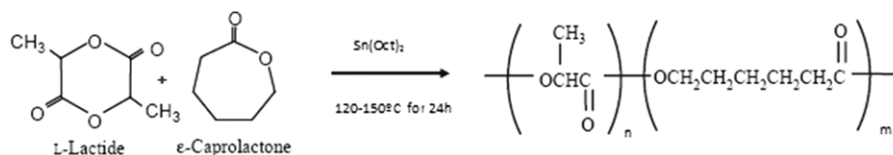


Fig. 1 – Scheme of the synthesis of PLCL statistical copolymers.

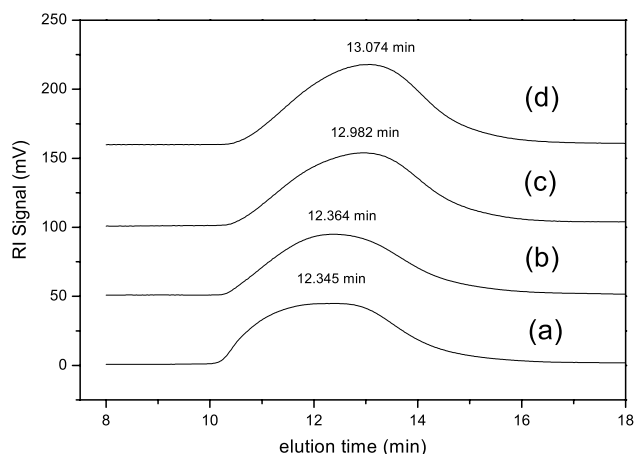


Fig. 2 – GPC curves of PLCL 9010 140 (a), PLCL 8020 140 (b), PLCL 7525 140 (c) and PLCL 7030 140 (d).

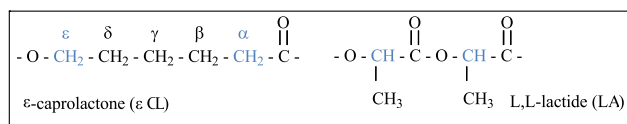


Fig. 3 – Scheme of the ϵ -caprolactone and L-lactide units.

curve, which indicates the successful copolymerization of LA and ϵ -CL.

Proton nuclear magnetic resonance spectroscopy

Proton nuclear magnetic resonance (^1H NMR) spectra were recorded in a Bruker Avance DPX 300 at 300.16 MHz of resonance frequency using 5 mm O.D. sample tubes. All spectra were obtained at room temperature from solutions of 0.7 mL of deuterated chloroform (CDCl_3). Experimental conditions were as follows: 10 mg of sample; 3 s acquisition time; 1 s delay time; 8.5 μs pulse; spectral width 5000 Hz and 32 scans.

The different signals of a ^1H NMR spectrum, shown in Fig. 4, can be easily assigned. The lactide methine gives the signal centered at 5.16 ppm, the signals around 4.1 and 2.35 ppm correspond to the ϵ and α methylenes of the caprolactone (see Fig. 3), respectively, and the rest of H are included in the signal between 1.7 and 1.3 ppm (not shown). These signals can be assigned to the different dyads of the PLCL (Kasperczyk and Bero, 1991).

It can be observed that both α and ϵ methylenes give two signals (two triplets). The triplets of the α and ϵ methylenes at the lowest chemical shift (δ), at 2.30 and 4.06 respectively, correspond to the CL–CL dyad, while the ones at lowest field (at 2.37 and 4.11) can be assigned to the CL–LA dyad

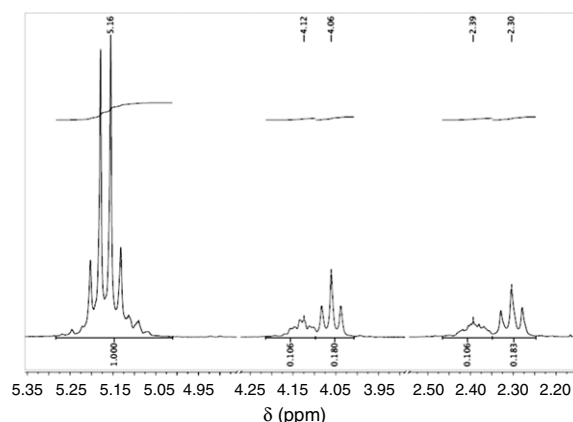


Fig. 4 – ^1H NMR spectrum of PLCL 8020 synthesized at 140 °C.

(henceforth, the underlining will be used to emphasize that the analyzed nuclei belongs to that unit). In the case of LA unit signals, the H–H coupling hinders to a large extent this type of analysis and the signals corresponding to LA–LA and LA–CL are overlapped in the LA methine signal at 5.16 ppm, even though the quartet at highest field, at ≈ 5.07 ppm, could be assigned to sequence LA–CL. Anyway, taking into account the fact that the LA–CL dyad contribution to the LA methine signal will take the same relative molar fraction obtained for CL–LA dyad, the experimental integration of the α and ϵ methylenes provides a way to calculate the total relative molar fraction of the CL–LA dyad. In this way, all the average dyad relative molar fractions could be calculated and, therefore, the copolymer composition and the microstructural magnitudes of the copolymers could be obtained from them.

Thermogravimetric analysis

Thermal degradation of PLCL copolymers was studied by means of thermogravimetric analysis (TGA) into a TGA model Q50-0545 (TA Instruments). Samples of 10–15 mg were heated from room temperature to 500 °C at a heating rate (β) of 5 °C min^{-1} , recording continuously the heat flow, sample temperature, residual sample weight and its time derivative. In this temperature range, the copolymers are degraded completely.

Mechanical characterization

Tensile tests were performed with an Instron 5565 testing machine at a crosshead displacement rate of 5 mm min^{-1} . The specimens for tensile tests were obtained from cast films of the PLCL synthesized at 140 °C. 175–225 μm films were formed by casting the chloroform solutions of the polymers followed by pressure melting at 175 °C and water quenching in order to achieve an amorphous state. The mechanical

Table 1 – Characterization of statistical PLCL copolymers of different compositions synthesized at various temperatures.

Sample	T °C	Feed mol. ratio		Copolym. compos.		Yield (%)	$M_n(\times 10^3)$ g mol ⁻¹	$M_w(\times 10^3)$ g mol ⁻¹	P.I.	T_g °C	T_m °C	ΔH_f J g ⁻¹	x_c %
		%LA	%CL	%LA	%CL								
PLCL 9010	120	87.7	12.3	91.8	8.2	89.5	102.9	199.8	1.94	57.3	173.7	29.6	29.9
PLCL 9010	130	87.7	12.3	89.0	11.0	89.4	106.3	215.6	2.03	53.7	169.9	35.1	36.4
PLCL 9010	140	87.7	12.3	89.8	10.2	90.0	104.7	226.0	2.16	54.6	162.6	35.0	36.0
PLCL 9010	150	87.7	12.3	88.5	11.5	83.5	64.6	113.1	1.75	44.7	155.6	30.2	31.4
PLCL 8020	120	76.0	24.0	85.0	15.0	83.5	77.8	132.2	1.70	46.8	167.9	27.0	29.0
PLCL 8020	130	76.0	24.0	80.9	19.1	89.2	105.8	186.8	1.77	44.2	163.8	30.0	33.6
PLCL 8020	140	76.0	24.0	77.7	22.3	90.3	96.0	181.4	1.89	35.5	155.9	26.7	31.0
PLCL 8020	150	76.0	24.0	77.3	22.7	84.8	65.4	110.7	1.69	29.7	150.1	26.2	30.4
PLCL 7525	120	70.4	29.6	80.0	20.0	81.8	71.2	98.5	1.38	41.6	167.0	27.4	30.9
PLCL 7525	130	70.4	29.6	74.1	25.9	90.2	99.0	184.7	1.87	39.9	158.8	25.7	31.0
PLCL 7525	140	70.4	29.6	72.5	27.5	88.2	82.1	147.2	1.79	26.4	147.9	22.0	27.0
PLCL 7525	150	70.4	29.6	70.0	30.0	80.9	62.6	105.7	1.69	23.4	141.9	21.2	26.7
PLCL 7030	120	64.9	35.1	75.9	24.1	81.7	76.4	121.4	1.59	34.9	158.3	20.0	23.7
PLCL 7030	130	64.9	35.1	69.6	30.4	84.8	75.7	133.7	1.77	32.6	157.8	21.8	27.7
PLCL 7030	140	64.9	35.1	66.4	33.6	85.1	78.1	137.8	1.77	19.3	146.0	20.3	26.8
PLCL 7030	150	64.9	35.1	65.7	34.3	86.1	68.1	117.7	1.73	16.4	137.2	15.7	20.9

properties were measured at 21 ± 2 °C and $50 \pm 5\%$ relative humidity (RH) following ISO 527-3/1995 (ISO 527-3/2/5), once the copolymer films were formed and after 5 weeks of storage at room temperature (21 ± 2 °C).

3. Results and discussion

Influence of synthesis conditions

Statistical PLCL copolymers were synthesized by ring opening polymerization at 120, 130, 140 and 150 °C, while the feed monomer composition of the synthesized copolymers was 90 : 10, 80 : 20, 75 : 25 and 70 : 30 (mass : mass ratio of LA to CL) on several mixtures of 20 g. The reaction was carried out for 24 h in the presence of stannous octoate and the comonomers:catalyst molar ratio was in all of them 2000 : 1. Other researchers employed comonomers:catalyst ratios of 1000 (Tsutsumi et al., 2009; Nalampang et al., 2007) or 200 (Jeon et al., 2003; Dechy-Cabaret et al., 2004) or a 0.2% w:w stannous octoate (Garkhal et al., 2007), utilizing in some cases 1-hexanol or glycols as initiators. However, the highest yields and molecular weights seems to be obtained with a 2000 : 1 comonomers:catalyst ratio (Lu et al., 2008). The copolymerization results are summarized in Table 1.

As can be seen, highest molecular weights and yields of reaction were obtained at 130 and 140 °C. The overall conversion of these PLCL copolymers was around 90% and they had a weight average molecular weight (M_w) between 133,000 and 226,000 g mol⁻¹. In addition, their polydispersity index (P.I.), which is a measure of the width of molecular weight distributions, was higher than the corresponding to PLCLs synthesized at 120 and 150 °C.

At temperatures lower than 140 °C, the incorporation of CL units into polymer chains was incomplete because of the low reactivity of CL (Jeong et al., 2004). Hence, at 120 °C the copolymerization was difficult to control (obtaining more LA in the copolymer than the desired) due to the fall of the CL reactivity. As an illustration, the molar lactide composition of PLCL 7030 120 was 76% when

a 65% was expected from feed composition. On the other hand, at higher temperatures the copolymer composition was closer to the feed composition because of the fact that the reactivities of the two comonomers were made equal. Nevertheless, at 150 °C the catalyst was less effective and the molecular weights of the copolymers took lower values. Another consequence of the higher reactivity of LA units during copolymerization, was that both number and weight average molecular weights of PLCL copolymers increased at higher LA content in LA : CL ratio.

Increasing the LA content in the feed, the glass transition temperature (T_g) and the melting temperature (T_m) approached to that of PLLA homopolymer, which usually shows a T_g at 55–65 °C and a T_m 170–183 °C depending on crystalline and rigid amorphous fraction development (Zuza et al., 2008). A value of 14 repeat units of lactide is reported to be the minimum sequence length for crystallization of polylactides (Sarasua et al., 1998) but in all PLCL synthesized in this work the average length of LA-unit sequences in the copolymer is large enough to form crystallites, taking into account that soft CL units enhance the mobility of LA domains allowing to LA blocks to arrange forming crystalline domains (Simic et al., 2000). However, the length of CL-unit sequences of the said copolymers was probed to be insufficient to allow their crystallization to occur. Hence, the crystallinity degree (x_c) in % was calculated from Eq. (1), having proven previously by X ray diffraction that only lactide units in PLCL 7030 are able to crystallize (Ugartemendia and Sarasua, 2011).

$$x_c(\%) = \frac{100 \Delta H_f}{\Delta H_f^0 \cdot (LA^*)}, \quad (1)$$

where $\Delta H_f^0 = 106$ (J g⁻¹ of PLLA) is the enthalpy of fusion of PLLA crystals having the infinite crystal thickness (Sarasua et al., 1998) and (LA^*) is the actual lactide mass fraction in the copolymer.

The copolymer compositions were measured by means of ¹H NMR spectroscopy. The ratio of the integrated intensity of the methine group of LA to the average value of the

Table 2 – ^1H NMR characterization of statistical PLCL copolymers of different compositions synthesized at various temperatures.

Sample	Average dyad relative molar fractions			Microstructural magnitudes of the copolymers				R
	(LA–LA)	(LA–CL)	(CL–CL)	l_{LA}	l_{CL}	$(l_{\text{LA}})_{\text{random}}$	$(l_{\text{CL}})_{\text{random}}$	
PLCL 9010 120	0.8898	0.0560	0.0542	32.79	2.93	12.20	1.09	0.37
PLCL 9010 130	0.8442	0.0926	0.0632	19.22	2.38	9.09	1.12	0.47
PLCL 9010 140	0.8438	0.1077	0.0485	16.67	1.89	9.80	1.11	0.59
PLCL 9010 150	0.8146	0.1398	0.0456	12.66	1.65	8.70	1.13	0.69
PLCL 8020 120	0.7751	0.1505	0.0744	11.30	1.99	6.67	1.18	0.59
PLCL 8020 130	0.7448	0.1278	0.1274	12.66	2.99	5.24	1.24	0.41
PLCL 8020 140	0.6943	0.1647	0.1410	9.44	2.71	4.48	1.29	0.48
PLCL 8020 150	0.6742	0.1979	0.1279	7.81	2.29	4.41	1.29	0.56
PLCL 7525 120	0.7253	0.1487	0.1259	10.75	2.69	4.99	1.25	0.46
PLCL 7525 130	0.6660	0.1496	0.1844	9.91	3.46	3.86	1.35	0.39
PLCL 7525 140	0.6264	0.1980	0.1756	7.32	2.78	3.64	1.38	0.50
PLCL 7525 150	0.5768	0.2472	0.1760	5.66	2.43	3.33	1.43	0.59
PLCL 7030 120	0.6705	0.1762	0.1533	8.62	2.74	4.15	1.32	0.48
PLCL 7030 130	0.6080	0.1753	0.2167	7.94	3.47	3.29	1.44	0.41
PLCL 7030 140	0.5614	0.2044	0.2342	6.50	3.29	2.98	1.51	0.46
PLCL 7030 150	0.5367	0.2411	0.2222	5.45	2.85	2.92	1.52	0.53

ε and α methylene signals of ε -caprolactone was used to determine the chemical composition of each copolymer. Moreover, taking into account that the random copolymer properties can be so different to the corresponding ones to a block or multiblock copolymer, the microstructure must be characterized. In this sense, some expressions have been proposed (Kasperczyk and Bero, 1991; Herbert, 1993). Applying Eqs. (2)–(4), the number-average sequence lengths (l_i) of LA and CL building blocks, the Bernoullian random number-average sequence lengths $(l_i)_{\text{random}}$ and the randomness character (R) are offered in Table 2.

$$l_{\text{LA}} = \frac{2(\text{LA})}{(\text{LA}-\text{CL})}; \quad l_{\text{CL}} = \frac{2(\text{CL})}{(\text{LA}-\text{CL})} \quad (2)$$

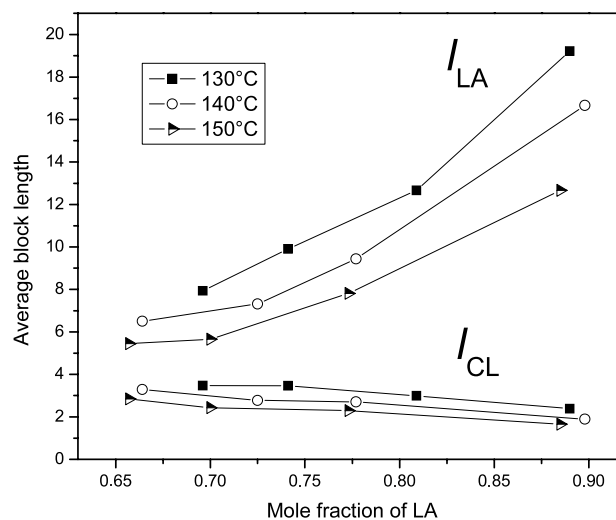
$$(l_{\text{LA}})_{\text{random}} = \frac{1}{(\text{CL})}; \quad (l_{\text{CL}})_{\text{random}} = \frac{1}{(\text{LA})} \quad (3)$$

$$R = \frac{(\text{LA}-\text{CL})}{2(\text{LA})(\text{CL})} \quad (4)$$

where (LA) and (CL) are the two comonomer molar fractions and (LA–CL) is the LA–CL average dyad relative molar fraction.

As well as the composition, the chain microstructure also affects thermal properties and crystallization. Fig. 5 presents the average length of CL and LA-unit sequences at 130, 140 and 150 °C. It can be observed that at higher temperatures the average length of LA-unit sequences is smaller. As a consequence, the T_g and the T_m of the copolymers shift to lower values and the crystallinity fraction is reduced.

Considering that in a block copolymer $R \rightarrow 0$ while in a random one $R \rightarrow 1$, it can be observed that all the synthesized copolymers took an intermediate value between the pure random (Bernoullian copolymer) and pure block copolymer; in this way, they showed moderate blocky character. Nonetheless, at lower temperatures a predominant formation of copolymers with higher blocky character was found. As can be seen in Fig. 5 and Table 2 the number average sequence lengths (l_{LA} and l_{CL}) were larger and the randomness character (R) value shifted from 0.4 at 130 °C to 0.6, at 150 °C. The multiblock character can be explained by the fact that the copolymerization rate of LA at lower

**Fig. 5 – Evolution of the average sequence lengths with the reaction temperature.**

temperatures was much faster than that of CL, so that LA monomers polymerized first to form blocks working as hard domains and the CL units reacted later to form the soft chain component of the copolymer.

In this work no copolymer with marked random character (above $R = 0.80$) was synthesized with stannous octoate in the range of 120–150 °C. Kricheldorf et al. (1992) observed that randomization is achieved in part due to transesterifications that can occur at high temperatures or at long reaction times. Moreover, the nature of the catalyst can affect the behavior of the copolymerization, affecting both the rate of the reaction and the sequence distribution of the comonomers and, in this sense, there have been some investigations onto various catalysts to improve the randomness of PLCL.

Fig. 6 presents the ^1H NMR spectra of PLCL 8020 130 and PLCL 8020 150. It can be observed that signals of the methylenes at the lowest field (at 2.39 and 4.12), which are assigned to the CL–LA dyads, are more intense in the case

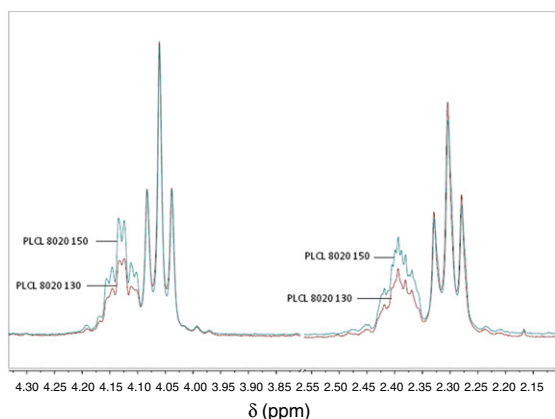


Fig. 6 – ^1H NMR spectra of PLCL 8020 130 ($R = 0.41$) and PLCL 8020 150 ($R = 0.56$).

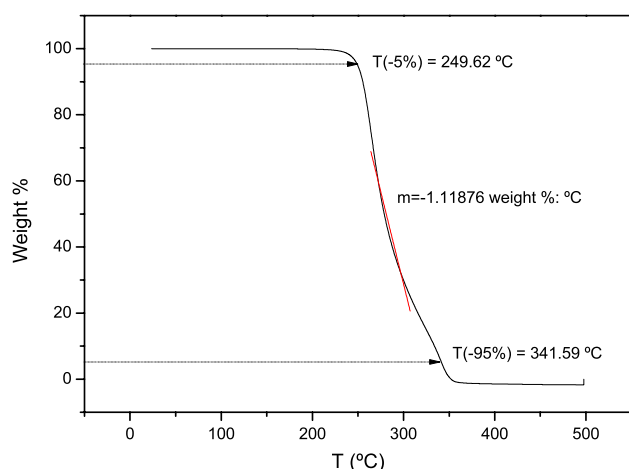


Fig. 7 – Thermogravimetric curve of PLCL 8020 140 at $5\text{ }^\circ\text{C min}^{-1}$.

of the copolymer synthesized at $150\text{ }^\circ\text{C}$ than in the one synthesized at $130\text{ }^\circ\text{C}$. The last one is the highest blocky copolymer of both of them with a R of 0.41.

Thermal degradation

The thermal degradation data are particularly important for processing polymers in the melt, especially where the final product is intended for use in a biomedical application. In this way, any thermal degradation byproduct formed during processing may be toxic to the human body. Moreover, the biomaterials could suffer a reduction in their mechanical properties limiting their applications.

The thermal stabilities of the copolymers synthesized at $140\text{ }^\circ\text{C}$ were studied by means of thermo-gravimetric analysis. TGA curves of PLCLs were obtained as in Fig. 7 representing the percent weight loss vs. temperature. The characteristic values from TGA curves (the temperatures corresponding to a 5 wt.% and a 95 wt.% weight loss, and the loss rate between 25% and 75% weight loss) were computed and can be viewed summarized in Table 3.

Based on the calculated rate of degradation, it is evident that the PLCLs degrade at a faster rate decreasing their CL content. Hence, the temperature in which the weight loss

Table 3 – Characteristic data of thermal degradation of PLCL.

Sample	T (–5% Weight loss) $^\circ\text{C}$	T (–95% Weight loss) $^\circ\text{C}$	Slope ^a $\frac{\% \text{ weight}}{^\circ\text{C}^{-1}}$
PLLA	261.3	312.3	–2.167
PLCL 9010 140	246.7	331.8	–1.444
PLCL 8020 140	249.6	341.6	–1.119
PLCL 7525 140	231.7	357.6	–0.796
PLCL 7030 140	247.3	365.1	–0.774

^aCalculated in the range of 75 to 25% of sample weight at the thermogravimetry curve.

is about 95% was higher in the high-CL copolymers. As an illustration, the PLCL 9010 degraded at 1.444% weight loss $^\circ\text{C}^{-1}$ and its temperature at 95% weight loss was $312.3\text{ }^\circ\text{C}$, while the degradation rate of the PLCL 7030 was 0.774% weight loss $^\circ\text{C}^{-1}$ and its calculated temperature was $365.1\text{ }^\circ\text{C}$. These results are in accordance with the well known studies that suggest that the PCL is more stable to thermal degradation than PLLA and that their copolymers have intermediate properties of thermal stability. On the other hand, although PLCLs started to degrade at lower temperatures than the PLLA, it was not found a noteworthy difference between the copolymers.

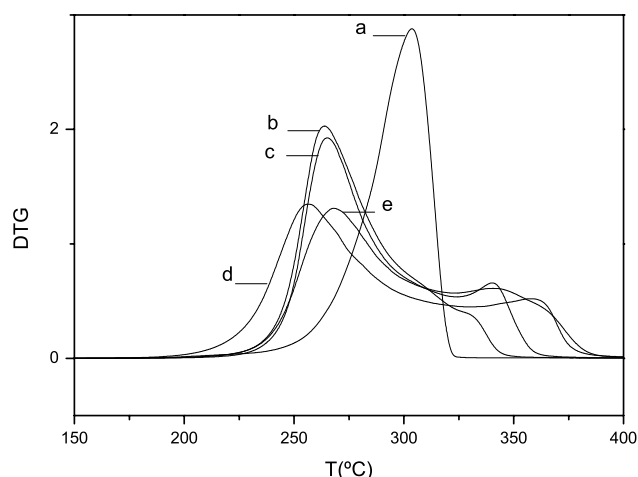
With regard to thermal degradation mechanisms, PCL degrades by both random chain scission and specific chain end scission mechanisms (Sivalingam and Madras, 2004) and PLLA by a multi step process that has been reported by Kopinke et al. (1996). In the PCL thermal degradation process random chain scission dominates at lower temperatures and as the temperature increases the specific chain end scission (from the hydroxyl chain end of the chain) becomes more important. In the case of PLLA, the dominant reaction pathway is an intramolecular transesterification, giving rise to the formation of cyclic oligomers. In addition, acrylic acid from cis-elimination as well as carbon oxides and acetaldehyde from fragmentation reactions were also observed. On the other hand, there is very little information about the degradation mechanism of PLCL copolymers.

The onset of thermal degradation in neat PLLA, in spite of exhibiting the fastest thermal degradation in regard to PLCL copolymers, is produced at a higher temperature than in PLCL copolymers. PLCLs follow two different stages of degradation. The lactide-rich sequences of PLCL degrade first, and later on the caprolactone-rich domains. However in the instance of neat PLLA the average sequence length of crystallizable lactide units is much larger leading to a higher and more compact crystalline fraction than in PLCLs, hence the onset of thermal degradation is delayed in neat PLLA because of the less accessibility of lactide units when arranged in close compact crystallite aggregates.

Fig. 8 shows the first derivative of the weight loss in TGA curves of the PLCL copolymers. At higher CL content, the peaks were broader and two different peaks were found for each copolymer pointing to a more complex degradation mechanism than those of the corresponding homopolymers. The first peak at around $250\text{ }^\circ\text{C}$ points to degradation of

Table 4 – Characterization of the films of the PLCLs synthesized at 140 °C conformed by melt solidification of solvent cast films.

Sample	Copolymer composition		M_n ($\times 10^3$) g mol ⁻¹	M_w ($\times 10^3$) g mol ⁻¹	P.I.	l_{LA}	l_{CL}	R
	%LA	%CL						
PLLA	100.0	0.0	261.3	426.8	1.63	–	–	–
PLCL 9010	90.0	10.0	81.5	172.7	2.12	17.24	1.91	0.58
PLCL 8020	77.8	22.2	76.1	144.5	1.90	9.76	2.79	0.46
PLCL 7525	72.8	27.2	73.8	138.7	1.88	7.30	2.74	0.50
PLCL 7030	66.3	33.7	73.1	131.1	1.79	6.29	3.19	0.47

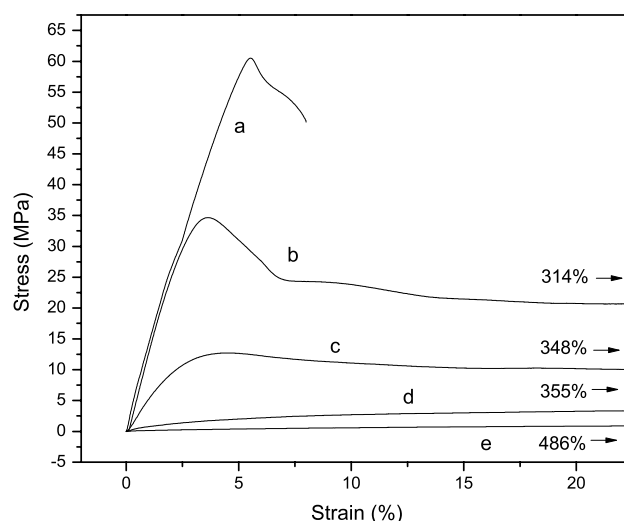
**Fig. 8 – Differential thermogravimetry curve of PLLA (a), PLCL 9010 (b), PLCL 8020 (c), PLCL 7525 (d) and PLCL 7030 (e).**

lactide-rich sequences with poor thermal stability. Then, in a second-stage of weight loss at about 350 °C the caprolactone-rich sequences, less sensitive to heat, are degraded (Nalam-pang et al., 2007).

Mechanical properties

Films of 175–225 μm thickness were prepared for mechanical testing by melt compression molding of previously solvent cast films. Briefly, chloroform solutions of the copolymers were cast onto a flat glass plate, followed by subsequent solvent evaporation. Then, to avoid any residual solvent induced plasticization and/or void type defects and achieve homogeneous defect-free amorphous samples for tensile testing, each of the cast films was placed between two sheets at 175 °C for 2.5 min and compressed under reduced pressure for 3 min. Finally, films were solidified from the melt by quenching in water at 15 °C.

The copolymers composition and the molecular weights were recalculated for the PLCL films since they could have undergone thermal degradation during melt conformation. Table 4 presents the ¹HNMR and GPC results showing composition, molecular weight and chain microstructure parameters of the copolymers studied. Comparing the films composition and average molecular weights of the copolymers resulting after melt processing to the values of the neat PLCLs of Table 1, it can be observed that the thermal treatment used for conformation affects the molecular weights but not the composition and microstructure (R) of the copolymers. Due to the different thermal resistance of LA and

**Fig. 9 – Stress-strain curves of the films of PLLA (a), PLCL 9010 (b), PLCL 8020 (c), PLCL 7525 (d) and PLCL 7030 (e). All PLCL copolymers were synthesized at 140 °C and tested just after conformation by melting and solidification by water quenching resulting in an amorphous structure.**

CL-unit sequences, changes in the copolymer composition were expected, however, after processing at 175 °C only some chain scissions at molecular level were detected, yet without any significant loss of weight. As expected, the copolymers containing lower contents of CL present worsened thermal stability, appear as more sensitive to the pressure melting, and thus undergo a significant loss of molecular weight in regard to their high CL copolymer counterparts. For instance PLCL 7030 did not undergo any change in molecular weight during processing at 175 °C.

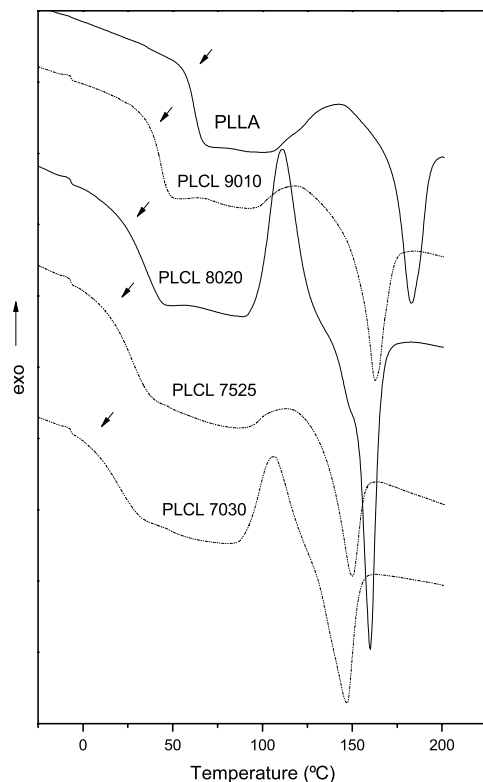
Fig. 9 shows the tensile stress-strain curves of PLLA and PLCL copolymers at 21 ± 2 °C. PLLA shows a typical curve for a glassy semicrystalline polymer with a prompt failure after yield point at $\epsilon_b = 8\%$ strain. In addition, since tensile tests were conducted at a testing temperature lower than its T_g , PLLA shows a quite stiff ($E = 1.7$ GPa) and strong ($\sigma_y = 51.9$ MPa) response. However, the shape of the tensile curves and mechanical properties of PLCLs are very different and depend greatly on copolymer composition.

Nascent PLCL 9010 resulting from polymerization at 140 °C presents a T_g at 54.6 °C and a crystalline fraction of 36%. However, after melt conformation, tensile samples of PLCL 9010 resulted basically amorphous. An increasing trend toward formation of a single amorphous phase was observed for PLCLs of higher CL content. As a result,

Table 5 – Mechanical properties of the PLCLs synthesized at 140 °C.

Sample	Elastic modulus ^a	Yield stress	Yield strain	Tensile strength	Elongation at break	Strain recovery
	(MPa)	(MPa)	(%)	(MPa)	(%)	%
PLLA	1665.5 ± 82.5	60.5 ± 1.0	5.86 ± 0.2	51.9 ± 3.6	7.96 ± 0.11	–
PLCL 9010	1343.1 ± 131.7	31.3 ± 3.8	3.47 ± 0.3	26.6 ± 2.5	314.2 ± 29.5	25.0 ± 1
PLCL 8020	506.9 ± 43.3	12.0 ± 1.4	4.76 ± 0.4	24.9 ± 1.6	347.6 ± 38.1	73.6 ± 3
PLCL 7525	61.1 ± 6.7	–	–	17.8 ± 0.7	354.8 ± 25.2	89.9 ± 3
PLCL 7030	12.0 ± 1.2	–	–	17.2 ± 0.7	485.8 ± 52.6	93.5 ± 2

^aThe elastic modulus provided for PLCL 9010 and PLCL 8020 is Young's Modulus and the elastic modulus provided for PLCL 7525 and PLCL 7030 is secant modulus at 2% strain.

**Fig. 10 – DSC curves of the copolymer films before mechanical testing.**

regardless the CL composition, they resulted amorphous after melt processing and their DSC revealed a very similar trace to that found for the second scan of the nascent polymers obtained after melting and rapid solidification in the DSC. Fig. 10 shows the DSC traces of PLLA and PLCL copolymers after conformation following melting and rapid quenching in water. All polylactides studied here showed a cold crystallization peak as a result of crystallization of LA building blocks during the DSC scan, however the neat enthalpy of fusion obtained was lower than 5% in all cases, demonstrating that tensile samples of PLCL copolymers after melt-conformation were basically amorphous. Hence the comparison of the mechanical behavior of PLCL copolymers is conducted in terms of copolymer composition, putting aside the small interference of crystallinity of PLCLs in tensile samples.

The analysis of the tensile curves of Fig. 9 demonstrates the high strain ability of PLCL copolymers showing strain at break values larger than 314.2%, in regard to PLLA that breaks just after yielding at a strain of 8%. The presence of CL units in lactide chains reduces also the stiffness and strength of PLCL. Moreover, a shift from a glassy-thermoplastic with a neat yield point to an elastomer-thermoplastic behavior (no yield point) was observed for PLCL copolymer compositions in excess of 22% CL, the CL content of PLCL 8020.

The mechanical properties corresponding to PLLA and PLCL copolymers are summarized in Table 5. It is remarkable that tuning the copolymer composition the elastic modulus of PLCLs can be reduced from 1343.1 MPa in PLCL 9010 to about 12 MPa in PLCL 7030. Significantly the elastomeric character of the copolymers also increases with CL content as is proven by the strain recovery values that shift from 25.0% in PLCL 9010 to 93.5% in PLCL 7030. These results demonstrate that mechanical properties of PLCL can be tuned by both adjusting composition during synthesis and a well controlled thermal process during manufacturing. However, PLCL structures resulting from melt solidification are metastable, i.e., prone to changes in supramolecular organization in function of time and temperature. Thus PLCLs can undergo significant physical aging, particularly when stored at temperatures close to the T_g as will be demonstrated in a later section.

It is remarkable that small amounts of CL in the copolymer are enough to produce large improvements in the strain ability of polylactide materials. In addition, meaningful changes in the strain recovery rate of the copolymers are observed with the addition of CL. PLCL 9010 and PLCL 8020 combine high deformation at break and high stiffness and seem to be very interesting materials in substitution of a rather brittle and stiff PLLA. On the other hand, high-CL copolymers as PLCL 7525 or PLCL 7030 display an elastomeric thermoplastic behavior which is a highly valued feature requested to polymers for some medical applications.

A CL content in polylactides in excess of 34% (the CL content of PLCL 7030) would still improve further the elastomeric character of PLCLs, however the glass transition temperature of the copolymers would evolve toward PCL's and the increased amorphous character would difficult their process ability. In addition, it is expected that copolymers having a marked random character (above $R = 0.80$) will display superior elastomeric properties than those of a rather blocky character, about $R = 0.5$, whose mechanical properties have been analyzed here.

PLLA at 21 °C is rather brittle and behaves as a glassy plastic, however PLCLs exhibit large elongation at break.

The high elastomeric character of PLCL copolymers are attributed to the multiblock chain microstructure where flexible soft segments alternate with hard crystalline blocks (Lu et al., 2008). In PLCL copolymers the crystalline PLLA domains hold the soft domains together in a network structure, serving as physical crosslink points that contribute to mechanical strength. Thus, higher average block lengths result in higher crystalline fractions contributing to increase the stress related properties (elastic modulus and strength). On the contrary, the introduction of CL units containing five methylene groups increases the chain flexibility leading to high chain mobility, reduced crystallization capability, low elastic modulus and high strain recovery (elastomeric behavior).

Physical aging

For conformation of reliable medical devices the manufacturers require a deep confidence on the material supply that must present stability, durability and predictability of the macroscopic and microscopic properties. Therefore, it is necessary to understand the changes that biopolymers undergo in their structure and mechanical properties during either the storage time before use or/and for long-term applications depending on temperature. This process by which the material tends to reach the equilibrium through the slow rearrangement of the polymer chains from this nonequilibrium glassy state is often referred to as physical aging.

Regarding PLCL, the studies of Tsuji et al. (2000); Saha and Tsuji (2006) demonstrated that these copolymers changed their physical properties during storage at room temperature. PLCL properties are not only the result of copolymer composition and chain microstructure features set during polymerization. A variety of supramolecular arrangements can be adjusted during its manufacturing. However, these are metastable phase structures that are prone to aging due to macromolecular changes occurring at mild temperatures and relatively short times (Ugartemendia and Sarasua, 2011).

In this work, in an attempt to study in more detail the aging effect of PLCL on its crystallization and physical properties, films of the PLCL copolymers synthesized at 140 °C (Table 4) were prepared and stored at room temperature (21 ± 2 °C). The glass transition temperature (T_g) and its associate specific heat change (ΔC_p), the enthalpy relaxation (δ_H) and its peak temperature (T_p), and the heat of fusion (ΔH_f) and the correlated melting temperature (T_m) and degree of crystallinity (x_c) were all monitored by means of DSC. The mechanical properties were measured after 5 weeks of storage.

In every copolymer film, the crystallization and crystalline region in the range of 143 to 160 °C is attributable to LA unit sequences, not CL-unit sequences (Ugartemendia and Sarasua, 2011). The average length of LA unit sequences in the copolymers is large enough to form crystallites during aging; whereas, the length CL-unit sequences seems to be insufficient for crystallization.

In the case of high-CL copolymers, the mobility of L-lactide unit sequences is enhanced by the presence of flexible CL units, resulting in a larger T_g drop. On account of this, PLCL 7030 was the copolymer which underwent the largest changes in its physical properties during aging. The storage temperature (21 °C) was lower than the corresponding T_g of

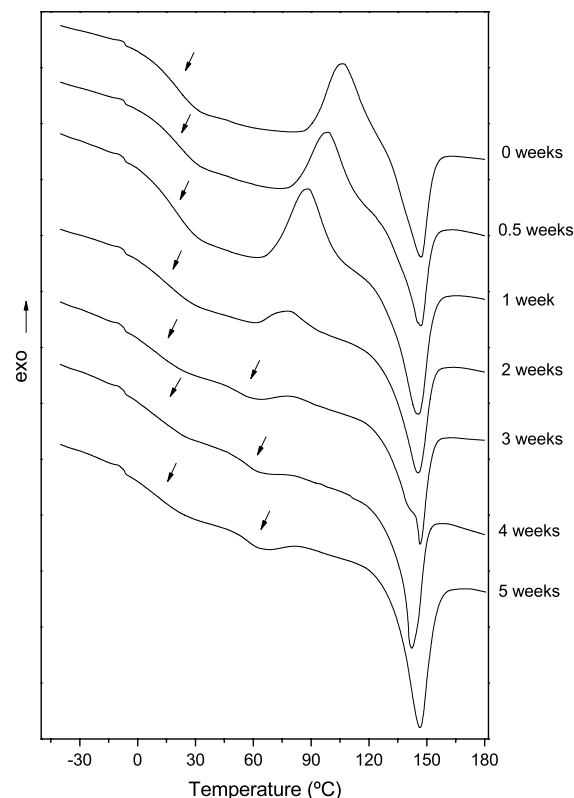


Fig. 11 – DSC scans of PLCL 7030 at different times of storage.

the PLCL 7525 (27 °C), PLCL 8020 (35 °C) and PLCL 9010 (44 °C) films. However, in the instance of PLCL 7030, the T_g (20 °C) and the storage temperature were similar so the mobility of the crystallizable chains in the amorphous phase might be clearly favored, making it possible the arrangement of lactide blocks in novel crystalline regions.

The DSC thermograms of the PLCL 7030 film stored for different times are shown in Fig. 11. Initially, the PLCL was completely amorphous which is inferred from the analysis of its DSC curve showing a recrystallization enthalpy approximately equal to that of melting, appearing at 146 °C. Aged PLCL 7030 samples show, however, the gradual disappearance of the recrystallization peak during storage, which is accompanied by the presence of a melting peak revealing the melting of polylactide crystallites developed during aging. As a result, the degree of crystallinity shifted quickly to 18% during the first two weeks of storage, reaching almost a value of 23% in the final week of the study. The crystallization slowed down in the final weeks and was almost completed in 5th week, meaning that the equilibrium was close. The whitening of the films during the storage was a visible feature indicative of physical aging.

The DSC scans of aged PLCL 7030 also show a double T_g behavior, which could be translated as a phase separation process. The single T_g of unaged PLCL 7030 at 20 °C shifted to lower values during aging while its associated ΔC_p slightly decreased. From week 3 of aging, a second T_g appeared at 48 °C and was risen until the ultimate value of 58 °C in the 5th week of storage. The lower T_g should be associated to

Table 6 – Mechanical properties of the PLCLs synthesized at 140 °C after 5 weeks of storage at room temperature.

Sample	Elastic modulus ^a	Yield stress	Yield strain	Tensile strength	Elongation at break	Strain recovery
	(MPa)	(MPa)	(%)	(MPa)	(%)	%
PLCL 9010	1471.0 ± 152.6	37.5 ± 2.1	3.72 ± 0.2	26.6 ± 2.7	300.9 ± 20.5	25.6 ± 2
PLCL 8020	574.1 ± 47.4	13.0 ± 1.2	4.74 ± 0.5	26.1 ± 2.3	347.5 ± 21.7	72.3 ± 3
PLCL 7525	91.3 ± 6.5	–	–	21.4 ± 1.9	349.8 ± 34.4	91.7 ± 1
PLCL 7030	128.5 ± 2.0	–	–	17.4 ± 0.4	397.4 ± 40.6	94.6 ± 2

^aThe elastic modulus provided for PLCL 9010 and PLCL 8020 is Young's Modulus and the elastic modulus provided for PLCL 7525 and PLCL 7030 is secant modulus at 2% strain.

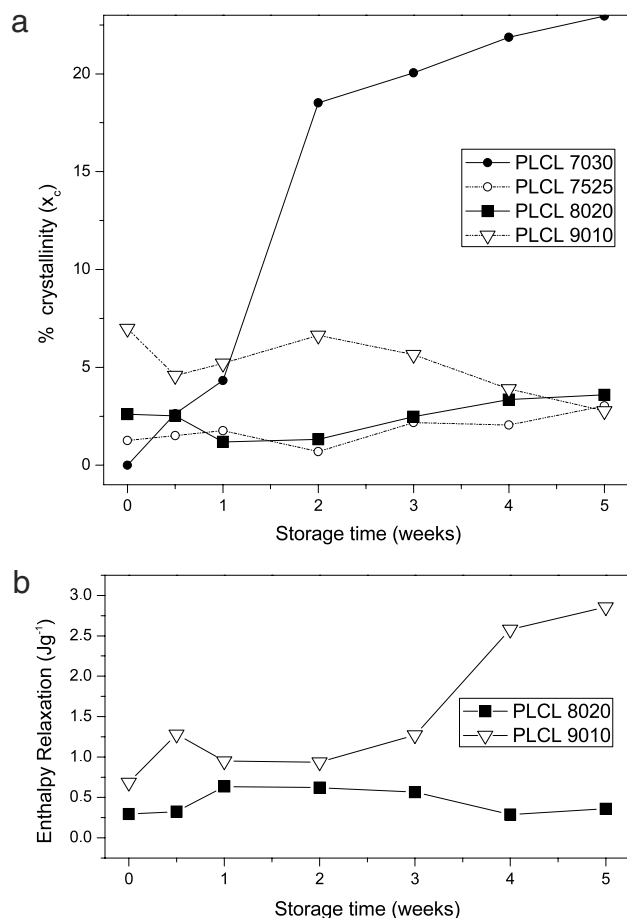


Fig. 12 – Evolution of % crystallinity (a) and the enthalpy relaxation (b) of the PLCL films during storage at room temperature. The x_c was calculated from previously discussed Eq. (1). The peak temperature of the enthalpy relaxations of PLCL 8020 and PLCL 9010 were respectively, about 46 and 50 °C.

the amorphous LA–CL phase, whereas the higher T_g suggests the presence of amorphous LA domains linked to the new crystalline phase resulting from the rearrangement of large enough LA building blocks during aging.

The other PLCLs containing larger amounts of LA did not suffer changes in T_g , T_m or ΔC_p , yet minor variations in their degree of crystallinity were observed. Fig. 12(a) presents the

evolution of the x_c of the PLCL copolymers stored at room temperature. The crystallization process during storage is limited due to the fact that the mobility of polymer chains is lower in these high-LA copolymers. As an illustration, in the PLCL 7525 the x_c was increased only until 3%. In the films of PLCL 8020 and PLCL 9010, these slight changes in crystallinity are accompanied with fluctuations in the enthalpy relaxation, which can also be appreciated in Fig. 12(b). The enthalpy relaxation peak at T_g reflects the decrease of specific free volume during aging that is on the basis of the increase of stiffness observed.

Physical aging could have had a pronounced effect on the mechanical properties of PLCL due to enthalpy relaxations and the formation of crystallites which act as points of reinforcement and constraints of the amorphous region domains between crystallites. Hence, mechanical properties of PLCL films were also measured after 5 weeks of storage. Fig. 13 presents the evolution of PLCL 7030 from being elastomeric to be a slightly glassy semicrystalline thermoplastic after 5 weeks of aging at 21 °C. Elastic modulus of PLCL 7030 rose from 12 to 128 MPa while its elongation at break was reduced. Surprisingly the elastic recovery did not change, for 94% was computed in both cases, indicating that elasticity is influenced by CL content rather than by phase structure evolution during aging.

The subsequent DSC scan after melting and rapid solidification in the DSC of the film aged for 5 weeks was very similar to the unaged scan presented in Fig. 10 and shows again a single T_g proving that the changes occurring during aging are reversible and are associated to the conformational changes leading to a novel supramolecular ordering and phase structure. Aging in PLCL is thus a physical process in which the evolution of structure cannot be associated to changes involving primary chemical bonding.

Comparing the results summarized in Table 6 for the aged samples to the data presented in Table 5 for the unaged, it can be concluded that only the PLCL 7030 undergoes dramatic changes in its behavior during aging. Elastic modulus, yield stress and tensile strength of the other PLCL films having higher LA content also shifted to higher values, but the variations observed during aging are not as significant as those related to PLCL 7030. Moreover, the elongation at break and the strain recovery were almost similar. In conclusion, a ϵ -caprolactone molar content below 22% (the CL content of PLCL 8020) seems to be enough to avoid the impact of physical aging at room temperature on mechanical properties of PLCL copolymers with a moderate blocky character $R \approx 0.5$.

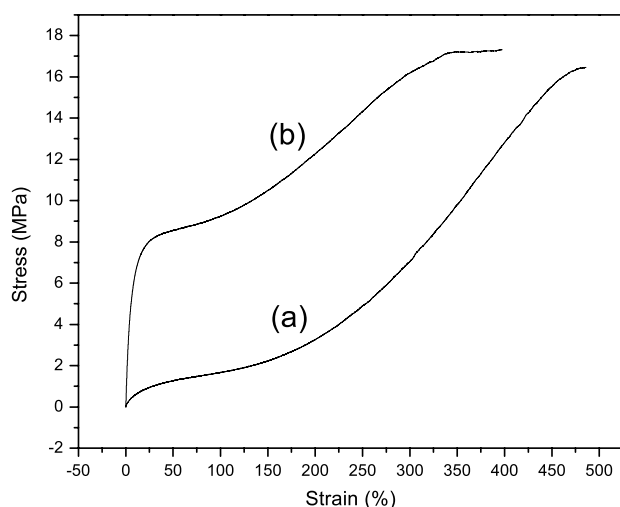


Fig. 13 – Tensile stress–strain curve of the films of unaged PLCL 7030 (a) and aged PLCL 7030 (b).

4. Conclusions

Synthesis of PLCL copolymers was carried out by ring-opening polymerization at 120, 130, 140 and 150 °C. The feed monomer composition of the synthesized copolymers was 90 : 10, 80 : 20, 75 : 25 and 70 : 30 (mass:mass ratio of LA to CL) on several mixtures, while the comonomers:catalyst molar ratio was in all of them 2000 : 1.

Highest molecular weights and yields were obtained at 130 and 140 °C. At 120 °C the reactivity of the CL falls and the polymerization was difficult to control (obtaining more LA in the copolymer than the desired). However, at higher temperatures the copolymer composition was closer to the feed composition. At 150 °C the catalyst was found to be less effective. Both the number and weight average molecular weights of synthesized PLCL copolymers increased at higher LA feed content in LA : CL ratio, due to the higher reactivity of LA units during copolymerization. At lower temperatures a predominant formation of copolymers with moderate blocky character was found; the number average sequence lengths (l_{LA} and l_{CL}) were longer and the randomness character (R), which took an intermediate value ($R \approx 0.4$ – 0.6) between the random ($R = 1$) and block ($R = 0$), was lower. Within the range of temperatures and compositions tried no marked random copolymer (above $R = 0.80$) was synthesized.

Increasing the LA content in the copolymers the glass transition temperature and the melting temperature approached to that of PLLA homopolymer. The crystallinity degree was also increased. Furthermore, the mechanical properties evolved in the same way toward the PLLA character, observing an increase in tensile modulus and a decrease in deformation at break when the molar content of LA was increased from 66% to 90%. Small amounts of CL content in the copolymers produced large improvements in their deformability. In addition, thermogravimetric analysis demonstrated that PLCLs are more stable to thermal degradation than PLLA and they undergo a more complex degradation mechanism than those of the corresponding homopolymers.

PLCL 7030 is the most affected copolymer by physical aging. After 5 weeks of storage at 21 °C, the degree of crystallinity of the initially amorphous film increased until a value of 23%. As a consequence, its mechanical properties evolved, e.g. the elastic modulus rose from 12 to 128 MPa, a yield point appeared at 8 MPa, strain at break decreased, while strain recovery after break surprisingly did not vary significantly. In the case of high-LA copolymers (above 78% of LA molar content), the mobility of LA unit sequences was hinted and subsequently aging effects were almost negligible.

Acknowledgments

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